

Abstract Title:

"H<sub>2</sub>O Adsorption Kinetics On Smectites"

RTOP # 344-30-11-02

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**Introduction:** The adsorptive equilibration of H<sub>2</sub>O with montmorillonite, a smectite clay has been measured. At low temperatures and pressures equilibration can require many hours, effectively preventing smectites at the martian surface from responding rapidly to diurnal pressure and temperature variations.

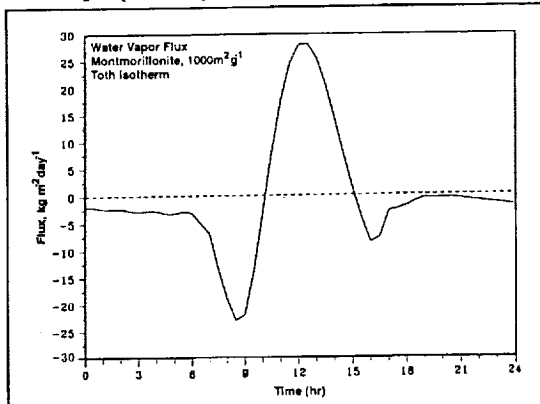
**Importance of Smectite Adsorption Kinetics:** Numerical models of the martian planetary boundary layer (PBL) assume instantaneous equilibration between adsorbed and vapor phase H<sub>2</sub>O. This assumption may not be valid for smectite clays. Some ground-based and spacecraft observations suggest that atmospheric H<sub>2</sub>O exchanges with the regolith daily. For example, Titov et al. (1995) argued that the Phobos 2 ISM instrument recorded daily variations in the H<sub>2</sub>O mixing ratio above the flanks of martian volcanoes. They argue that the atmospheric H<sub>2</sub>O column, observed during the day, is  $5 \pm 2$  times the column observed over the surrounding plateaus. They advanced the hypothesis that surface clays on the flanks of the volcanoes, experiencing significant diurnal exchange with the atmosphere, were responsible for the apparent increase in the H<sub>2</sub>O column abundance above the volcanoes.

Sprague et al. (1999) have also argued that telescopic observations, even when corrected for atmospheric scattering, show distinct, repeatable, and substantial diurnal variations in water abundance. This confirms work produced by the same group, as well as by Barker (1997).

Other observations and models have yielded different results. Titov et al. (1999), observing the martian atmosphere from the Pathfinder IMP cameras reported that water vapor seemed primarily confined to a layer in the lowest 1-3 km of the atmosphere, and showed no significant morning to evening variations in abundance. Davies (1979) also suggested that no conclusive evidence of diurnal H<sub>2</sub>O exchange was observed in Viking data. From a modeling perspective, Zent et al. (1993) argued that the Martian boundary layer must collapse in the mid-afternoon, when surface temperatures drop below atmospheric temperatures. The resulting thermal stabilization of the lowest atmosphere effectively strands most of the atmospheric H<sub>2</sub>O column at altitude, and prevents significant diurnal exchange.

One possibility for establishing rapid diurnal variations in the atmospheric H<sub>2</sub>O column is to use a very high-capacity adsorbent at the base of the

atmosphere. Numerical simulations of the PBL suggest that very substantial amounts of H<sub>2</sub>O can exchange between atmosphere and surface during the daylight hours, providing that the high-capacity adsorbent can remain in equilibrium with the rapidly changing conditions of temperature and H<sub>2</sub>O partial pressure. Smectite clays are the



favored high-capacity adsorbent for Mars.

The keys to resolving these issues are: a) how much smectite is available, and b) how quickly does it equilibrate with its pore gas? We set out to answer the second question here.

#### Smectite Adsorption

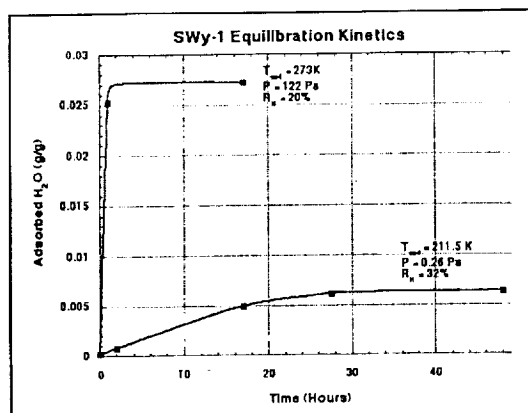
A few percent of smectite in the soil will dominate H<sub>2</sub>O adsorptive behavior of the regolith. The reason for that is the availability of interlayer sites to adsorb a considerable amount of H<sub>2</sub>O. That amount of clay is still allowed by available constraints. Christensen et al. (1998) reported upper limits of <20% for clay minerals in the Hebes Chasma area. Smectites have interlayer sites accessible by H<sub>2</sub>O. Typical BET surface areas using H<sub>2</sub>O molecules as probes are in the range of 10<sup>2</sup> to 10<sup>3</sup> m<sup>2</sup> g<sup>-1</sup>. Conversely, the BET surface area using N<sub>2</sub>, a non-polar molecule that cannot access interlayer sites, are a few 10<sup>1</sup> m<sup>2</sup> g<sup>-1</sup>. Montmorillonite, if it equilibrates rapidly, could play a significant role in buffering possible large magnitude exchanges of H<sub>2</sub>O.

#### Experiment Design

We are characterizing the kinetics of smectite adsorption under Mars-like conditions. We determine this experimentally by first dehydrating samples of SWy-1 a Na-montmorillonite, and then equilibrating them to Mars-like conditions for prescribed periods of time, and noting approach to equilibrium load.

Approximately 100 mg samples were baked out at 220°C for 1 hour under vacuum before the experiments, to remove as much H<sub>2</sub>O as possible..

As in standard adsorption measurements, the samples are then equilibrated at low T with water vapor. We control the partial pressure of water in the manifold by buffering ice at a temperature slightly below that of the soil, providing R<sub>H</sub> on the order of 0.2 – 0.5. Soil and ice temperatures are controlled by



immersion coolers, which have stability no more than  $\pm 0.5$  C. Therefore, we cannot achieve R<sub>H</sub> greater than about 50% without risking saturation in the soil sample. Samples are allowed to equilibrate for various amounts of time, then are sealed and removed from the manifold. Samples are carried to gas chromatograph without breaking seal, heated to 220°C and trapped under LN<sub>2</sub> for 1 hour. This effectively transfers all the adsorbed H<sub>2</sub>O from the soil to a clean glass trap. The traps are then heated with wire wrap and manifold heaters to approximately 100 °C to vaporize all of the H<sub>2</sub>O. On injection, the column temperature is 140°C, and the thermal conductivity detector is at 160°C.

During calibration, soil samples were baked out, and trapped with no exposure to H<sub>2</sub>O. Typical counts were on the order of 10<sup>3</sup>. In experiments with equilibration, signals were on the order of 10<sup>4</sup> to 10<sup>5</sup>, a full order of magnitude (at a minimum) above the background. In order to calibrate the system, Mg, Na, and Li chloride solutions were used. These solutions provide number densities in the vapor phase that are similar to the expected values from the adsorbate.

#### Equilibration Timescales

The results to date are shown in Figure 2. There is clearly a kinetic barrier to equilibration as a function of temperature. At 273 K, and RH = 0.2, the system

appears to equilibrate in under 1 hour. However, at 211K with RH of 32%, the sample requires approximately 26 hours to reach its equilibrium adsorbate population. Additional data are being acquired at temperatures of 273 K, but with extremely low RH (approx. 0.05) to see how rapidly equilibration occurs under those conditions which are representative of the near surface regolith during the day.

We will also be addressing the kinetics of desorption in samples under Mars-like conditions.

#### Discussion and Summary

Plainly, numerical models of the PBL will need to account for the kinetic barriers to equilibration in smectite clays, should they prove to be present in even small percentages in the Martian regolith.

In particular, there remains concern about whether smectite clays undergo interlayer under Mars-like conditions. It has been argued (Koster van Groos and Guggenheim, 1984) that once interlayer collapse occurs in smectites that they are virtually impossible to rehydrate. Therefore, the state of the interlayer H<sub>2</sub>O in smectites under mars-like conditions becomes a significant question.

In any event, smectite clays are unlikely to account for putative large diurnal variations in atmospheric H<sub>2</sub>O. In the first place they do not appear to equilibrate rapidly enough with the pore gases at Mars-like conditions. Secondly, any putative concentration of clay-like minerals would quickly lose it's charge of H<sub>2</sub>O due to atmospheric transport to other, more clay-poor sites.

The favored hypothesis for the diurnal variations observed by Titov (1995) and Sprague et al (1999). Colburn et al (1989) reported diurnal variations in optical depth, which supports the hypothesis that a measurable fraction of the atmospheric H<sub>2</sub>O column condenses diurnally on aerosols. Further supporting this hypothesis is the observation by Sprague et al (1999) that the apparent diurnal H<sub>2</sub>O variation is maximized during heavy atmospheric dust loading.

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